MTL TR 91-53

AN EXAMINATION OF PROCESSING VARIABLES IN THE PULTRUSION OF GLASS REINFORCEMENTS WITH AN EPOXY-ANHYDRIDE RESIN SYSTEM

DONALD J. JAKLITSCH, MARIA T. BOSTIC, and
ELIAS R. PATTIE
COMPOSITES DEVELOPMENT BRANCH

December 1991

US ARMY
LABORATORY COMMAND
MATERIALS TECHNOLOGY LABORATORY

U.S. ARMY MATERIALS TECHNOLOGY LABORATORY
Watertown, Massachusetts 02172-0001

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: MTL TR 91-53

2. GOVT ACCESSION NO.:

3. RECIPIENT'S CATALOG NUMBER:

4. TITLE (and Subtitle): AN EXAMINATION OF PROCESSING VARIABLES IN THE PULTRUSION OF GLASS REINFORCEMENTS WITH AN EPOXY-ANHYDRIDE RESIN SYSTEM

5. TYPE OF REPORT & PERIOD COVERED: Final Report

6. PERFORMING ORG. REPORT NUMBER:

7. AUTHOR(s): Donald J. Jaklitsch, Maria T. Bostic, and Elias R. Pattie

8. CONTRACT OR GRANT NUMBER(s):

9. PERFORMING ORGANIZATION NAME AND ADDRESS:
U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
ATTN: SLCMT-MEC

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:
D/A Project: 1L262105AH84
AMCMS Code: P612105.H84

11. CONTROLLING OFFICE NAME AND ADDRESS:
U.S. Army Laboratory Command
2800 Powder Mill Road
Adelphi, Maryland 20783-1145

12. REPORT DATE: December 1991

13. NUMBER OF PAGES: 27

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office):

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Composites
Epoxy resins
Polymer composites
Pultrusion
Processing variables
Pultrusion variables

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

(SEE REVERSE SIDE)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Block No. 20

ABSTRACT

Three stages of the pultrusion process were investigated for potential value in process control. Collectively, they represent the three major steps necessary for the manufacture of composite materials by pultrusion: fiber dispensation, resin application, and resin cure. The purpose was to determine whether the processing conditions imposed by each of these steps have a direct correlation to the physical properties exhibited by the final product.

In order to examine the first two stages, a series of experiments were conducted involving the process components which precede the raw materials entry into the heated die. Specifically, these were the fiber tension as adjusted in the creels and the viscosity of the resin in the bath as a function of time. The third stage of the process was studied through a series of experiments designed to gauge the effect of varying the processing parameters associated with the heated pultrusion die which are the line speed and die temperature.

The experimental results were evaluated by examining variation in mechanical properties of pultruded stock as produced under the various sets of conditions. Short beam shear and flexural tests were performed and measurements of product density, degree of cure, and void content were made. The results provide a solid empirical knowledge base for the process and a relative ranking of importance of the three stages in a control strategy.

CONTENTS

INTRODUCTION

A cursory overview of the pultrusion process leaves the observer with an impression of a process marked by its simplicity. A closer examination, however, reveals this assumption to be faulty as evidenced by the lack of development of a robust control system. The pultrusion process can be divided into four main components which roughly correspond to the machine parameters. For wet pultrusion, the processing method investigated herein, these correlate to fiber dispensation, resin application, resin cure, and a pulling system which incorporates a cut-off station.

Three stages of the process were selected and evaluated for their potential as areas of control. In machine terms, they are the creels, resin bath, and heated die. They were studied to determine whether the processing conditions imposed by each had a direct correlation to the physical properties exhibited by the final product.

In order to examine the first two stages, a series of experiments were conducted involving those components prior to the die. In these, the effects on mechanical properties of the fiber tension, as adjusted in the creels, and the viscosity of the resin in the bath were considered. The third stage of the process was investigated through a series of experiments on the effects of varying processing parameters most closely associated with the heated pultrusion die. This latter group of experiments examined the resultant mechanical properties of pultruded parts processed under various combinations of line speed and die temperature.

BACKGROUND

Fiber Tension

One of the chief benefits of producing composites by pultrusion is the preloaded state of the product attributable to the constant fiber tension during fabrication. The magnitude of this may affect the product's mechanical properties. In 1987 Arnold and Tessier[1] developed a low cost device to control individual tow tension. This device was developed for use with high modulus graphite fibers dispensed from center wrapped packages enclosed in plastic bags. Arnold and Tessier became aware of the importance of maintaining proper fiber tension during processing when ballooning occurred at the preform entrances. This resulted in misalignment of the tows prior to the die entrance and in some cases rupture of fibers which ultimately halted the process. Included in their study is an examination and evaluation of the application of standard tensioning devices to the pultrusion process, all of which proved ineffectual. Their solution was to build an adjustable aluminum frame into which a series of polyethylene tubes were installed. These tubes were bent to provide curved paths which effectively controlled tow tension.

In the present study, examination of the effects of fiber tension was made using S2 glass as the reinforcement material, and was motivated in part as a result of problems encountered during the die threading operation. In a situation analogous to that described by Arnold, the S2 glass tows migrated and intermingled within the die. This resulted in fiber disruption and destruction and ultimately, die seizure. In some cases, there was slippage of one or more of the tows making up a reinforcement tier. In others not all of the filaments constituting a tow progressed at the same pace, indicating the existence of a threshold of fiber tension, below which satisfactory procressing is impossible. In order to ascertain the value of this threshold, the techniques and the device designed by Arnold and Tessier were adopted.

1. ARNOLD, E. S., and TESSIER, N. J. *A Simple, Low Cost Tensioning Device for Pultruding Composite Materials.* The 32nd International SAMPE Symposium, v. 32, California, 1987.

Resin Bath Viscosity

The role of resin viscosity in pultrusion has been correlated to internal die pressure,[2] pulling force (shear forces in the die)[3] and process faults such as birds nests. Birds nests are described as reinforcement build ups around the die entrance which ultimately results in failure within the die. They have been attributed to high resin viscosity and excessive resin pick up.[4]

Clearly, controlled resin pick-up and fiber wet-out are vital to successful pultrusion processing. Process concerns such as cure time and maximum exotherm temperature depend upon the amount of resin carried into the die, while optimum properties such as strength require adequate fiber wet-out.

Schott et al.[5,6] dealt specifically with resin pick-up and fiber wet-out in both polyester and epoxy pultrusion using three reinforcement types, glass, kevlar, and graphite. The epoxy resin was the same as that employed in this work. Schott's approach in this research was to apply the case of the free withdrawal of a cylindrical solid rod from a quiescent resin bath in which the layer of liquid remaining on the rod is dependent on the viscosity and surface tension of the resin, as well as the speed of withdrawal. In this type of analysis the resin would be dragged along the fibers in two ways, via viscous drag or capillary forces. Viscous drag is dependent upon viscosity, density, and line speed while penetration due to capillary forces is dependent upon surface tension, fiber packing, and line speed.

The results of the study on the polyester resin (see Reference 5) demonstrated that in both cases (fiber bundle coating and/or penetration) the amount of resin pick-up and/or fiber wet-out was dependent upon the line speed and resin viscosity. This implies that any optimization for part quality must consider resin viscosity and line speed.

This was not the case in the studies performed with the epoxy resin system (see Reference 6) where results demonstrated that the coating weight was independent of line speed. It was concluded that this was due in large part to the very low surface tension of the epoxy resin resulting in a relatively large capillary number. This, coupled with the fact that increases in viscosity only serve to increase the value of the capillary number insures that the capillary number does not fall below the critical value at which coating weight changes with line speed. The authors have pointed out, however, that the application of this analysis to the interior of the fiber bundle may be limited since within the bundle there may be variatons in wet-out due to resin viscosity.

Die Temperature and Line Speed

The relationship between the heated die and line speed can be viewed in terms of an irreducible coupling between physical and chemical factors essential to the process itself. Boudart[7] has described this phenomena in chemical kinetics using the analogy of methane burning in the flame of a bunsen burner. The methane reacts at a rate which is determined by physical and chemical processes that could be uncoupled only by destroying the flame. This inability to separate the coupling of heat diffusion and the chemical kinetics of the thermosetting resin characterizes the heated die of the pultrusion process.

2. SUMERAK, J. E. *Understanding Pultrusion Process Variables.* Modern Plastics, v. 62, no. 3, 1985.
3. PRICE, H. L., and CUPSCHALK, S. G. *Pulling Force and Its Variations in Composites Material Pultrusion* in Polymer Blends and Composites in Multiphase Systems, C. D. Han, ed., Advances in Chemistry Series, 206, American Chemical Society, 1984.
4. GIBSON, A. G., LO, C. Y., LAMB, D. W., and QUINN, J. A. *Understanding the Factors Controlling the Pultrusion Process.* Plastics and Rubber Processing Applications, v. 12, no. 4, 1989.
5. DHARIA, A. N., and SCHOTT, N. R. *Resin Pick-Up and Fiber Wet Out Associated with Coating and Pultrusion Processing.* Antec 44th Annual Technical Conference, Boston MA, 1986.
6. NAKAYAMA, T., and SCHOTT, N. R. *Resin Pick-Up and Fiber Wet Out in the Pultrusion Process.* First Japan International SAMPE Symposium, Chiba, Japan, 1989.
7. BOUDART, M. *Kinetics of Chemical Processes.* Prentice Hall Inc., New Jersey, 1968, p. 144-145.

The transport phenomena which occur in the pultrusion die can be described as a unit process, however, in terms of the rate of the exotherm and the location at which it occurs in the die. A very slow exotherm causes the part to have poor surface quality due to spalling and sloughing.[8] An exotherm occuring very quickly is characterized by uneven and uncontrolled heating, which produces voids and, in some cases, depending upon the resin induces internal cracking due to stress relief. An important aspect of this study is to determine the effects of line speed and die temperature on the resulting degree of cure, as evaluated through the mechanical properties of the pultruded stock.

EXPERIMENTAL OVERVIEW

The system formulating selected for this study consisted of 100 parts Epon 826 resin, a DGEBA, (Diglycidyl) Ether of Bisphenol A manufactured by Shell Chemical Compay), 80 parts MTHPA (Methyl Tetrahydro Phthalic Anhydride manufactured by Anhydrides and Chemicals, Inc.) as the hardener and 1 part BDMA (Benzyldimethylamine manufactured by Miller Stephenson Chemical Company, Inc.) as the accelerator, in conjunction with an internal mold release (Ceara HT-1, made by Ceara Products Inc.) at 1.5% of total weight and a viscosity modifier Zeothix 265 (a precipitated amorphous silica, produced by J. M. Huber Corporation) at 2.5% of the total weight. Both E and S-glass fiber rovings treated with an epoxy-compatible sizing were used to produce pultruded stock having calculated theoretical fiber volumes of 65%.

The pultrusion equipment used at this laboratory is a Goldsworthy Glastruder. Rovings are dispensed from a creel, containing the tows either in large center wrapped packages or on individual spools which then pass through a carding rack and into a two-gallon resin bath. The original resin bath was replaced with a smaller bath in order to facilitate short runs. Upon leaving the bath the fibers pass through a set of Teflon® rollers, designed to squeeze out excess resin, and into a series of three Teflon® preformers. The preformers, spaced at two-foot intervals, aid in resin wet-out. Emerging from the last preformer, the fiber bundle has the desired wet-out and approximate shape and enters the heated die. The die used in this study is 30 inches long and produces rectangular stock of a 1/4- x 1-inch cross-sectional area. Die heating is accomplished by means of induction heaters positioned at three zones along the die length. The heaters are controlled through thermocouples imbedded in the die at approximately the center position of each temperature zone. In situ temperature data was acquired using an industrially hardened IBM PC-AT computer in conjunction with a Cyborg Loggernaut® data logger. Thermocouples were implanted within and on the surface of the fiber mass just prior to its entry into the die. The exact position of these sensors was determined when the specimens were cut during post processing analysis.

The post processing analysis included a series of tests which were conducted to analyze the effects that processing parameters had in relation to the pultruded stock's physical and mechanical properties. These tests included density measurements, ignition tests to determine actual fiber/resin content, determination of the cured composites' glass transition temperature, flex bar, and short beam shear tests.

Density measurements were made using a pycnometer which calculates the volume of a specimen from the weight of the water it displaces. The fiber/resin content of the pultruded stock was evaluated using methods based on ASTM D 2585-68 (reapproved 1985), the standard test method for ignition loss of cured reinforced resins. This method involves comparison of sample weights prior to and subsequent to, the resin being burned off in a 550°C muffle furnace. The data from these experiments were used to

8. JAKLITSCH, D. J., BOSTIC, M. T., and WALSH, S. M. *An Analysis of the Effect of Processing Conditions on the Microstructure and Resultant Mechanical Properties of Pultruded Stock.* The 34th International SAMPE Symposium and Exhibition, 1989.

evaluate the void content of a composite through a comparison with the calculated theoretical density of the material. The glass transition temperature, which is often used to provide an indication of the crosslink density, was measured using differential scanning calorimetry (DSC).

An ASTM test method to determine the flexural properties of the pultruded stock was also employed. The method, from ANSI/ASTM D 790-71 (reapproved 1978), employs a three-point loading system using center loading (a 1/2-inch nose) on a simply supported beam. In this configuration, the maximum axial fiber stress occurs on a line under the loading nose. The three-point bending method has a history of use in quality control and in defining specifications. The nominal quarter-inch stock was cut to a width of one-half inch and a length of 10 inches. This corresponds to a support span-to-depth ratio (L/D) of 32 to 1 including a one-inch overhang.

Short beam shear tests were also performed using a fixture as described in ASTM standard D 2344-76, A span to thickness ratio of 5 to 1 was accomplished through a 7 to 1 length to thickness ratio in a specimen with dimensions of 0.25 inches wide by 0.25 inches by 1.75 inches. The specimen ends rest on two supports and the load is applied by means of a loading nose that is centered directly on the midpoint of the test specimen.

All samples were tested in an as-is condition, that is none of the samples received post-cure treatments. The absence of post-cure, as well as certain characteristics inherent to composites produced some testing problems, for example, all short beam shear samples failed in bearing. In the case of the flexure tests none of the S2 glass samples failed in tension, while the E glass samples failed in both bearing and tension.

The lack of consistency in the failure mode prevents one from calculating certain properties, for example, the flexural strength. It is permissable, however, to make the calculations for use in data comparison. In the case of the materials tested here, the maximum load was used to calculate a maximum shear and flexure stress and should be interpreted not as a material property but as a physical response.

Tension

The S2 glass used in the tension experiments was dispensed from large (approximately 30 pounds) center wrapped packages, contained in cardboard boxes and positioned on tiers in the creel. Each tow was drawn through a plastic funnel mounted over the center of the package. This served to minimize package-to-package variations in tension by insuring that the tows did not contact the sides of the box and were consistently pulled from the center of the package.

After passing through the funnels, the tows were passed through polyethylene tubes which could be bent to alter the drag (tension) on the fibers. These tubes were mounted on the tiers at the front of the creels and were 18 inches long with respective outside and inside diameters of 3/8 inch and 1/4 inch. They were secured at either end by machined aluminum bar stock linked by two threaded rods. The rods were used to adjust the distance between the frame ends which in turn created the bend in the tubes.

To insure that the tension of the fiberglass reinforcement could be controlled as it had been for graphite, a simple experiment was carried out. A known length of tow was pulled through the tensioning device, weights of various sizes were hung from the tow and the sag from the baseline to the weight was measured. This procedure was carried out for tubes with no curvature, and tubes with a radius of 5-1/2 inches. The results, illustrated in Figure 1, demonstrate that variation of tension in the fiberglass tow could be accomplished by this arrangement.

This device was used to provide the three different tow tensions used in this study. In these experiments, full tension corresponds to tension imposed by a bend with a radius of 5-1/2 inches, half tension by a radius of 3-1/4 inches, and "zero" or "no tension" by tubes with no curvature. A laboratory pull spring scale was used to measure the drag force added by the tubes at each of these settings. The straight tubes added 0.3 Newtons per tow, tubes bent for half tension added 1.5 Newton/tow and those bent for full tension provided an extra 4 Newtons/tow. Since 127 tows were used, the total increase in force was 38.1, 190.5, and 508 Newtons, respectively, for each of the three settings.

The addition of tension immediately produced noticeable results on the threading up procedure. The "zero tension" condition allowed for a much easier thread up procedure, whereas full tension increased the difficulty of the threading operation. Increases in tension also appeared to decrease the tolerance of the system for changes in line speed or die temperature set points once steady state had been achieved. Consequently, only one run was made at the highest tension level due to the extreme adversity encountered in the run which terminated as a result of die freeze up.

Immediate examination of the opened die showed large areas of heavy resin build up on the die surfaces in differing locations on the top and bottom halves of the die indicating an unstable and uneven gel zone. This may be indicative of increased importance of misalignments existing in the system under conditions of full tension. For example, if the top half of the die cavity is below the natural line of the fiber/resin bundle as it stretches between the resin bath and the pullers, the increased contact with the upper portion of the die will increase the sensitivity of the process to the positon of the surface gel zone, and especially to any movement of the gel zone.

The tension experiments were run at different combinations of two line speeds and two die temperature profiles which represent the set points of the control thermocouples. The experimental scheme is outlined in Table 1.

The effects of the machine parameters on the pultruded product were evaluated by results of mechanical testing. Flexure tests were performed on 10 samples while 20 samples were tested by the short beam shear test. All samples were taken from randomly selected portions of pultruded stock produced under the conditions of interest and averaging 30 feet in length. The results of these tests are shown in Table 2. Means are reported with the standard deviation given below in parentheses.

Table 1. MACHINE PARAMETERS FOR THE FIBER TENSION EXPERIMENT

Case	Tension	Line Speed (in./min)	Die Temp. (°F)
1	Full	6	330
2	Half	6	330
3	Half	6	350
4	Half	9	350
5	None	6	330
6	None	6	350
7	None	9	350

Table 2. MECHANICAL PROPERTY DATA FOR TENSION EXPERIMENTS

Case	Tension	Temp. (°F)	Line Speed (in./min)	Flex Stress (psi)	Flex Modulus (ksi)	Max. Shear Stress (psi)
1	Full	330	6	173,232 (±4221)	7,928 (±146)	9,275 (±187)
2	Half	330	6	176,856 (±7084)	8,039 (±151)	9,298 (±168)
3	Half	350	6	179,881 (±6012)	8,099 (±147)	9,560 (±229)
4	Half	350	9	176,567 (±7032)	7,894 (±128)	8,936 (±316)
5	None	330	6	178,989 (±7029)	7,842 (±142)	9,403 (±270)
6	None	350	6	173,138 (±7720)	8,069 (±144)	9,530 (±152)
7	None	350	9	177,085 (±5130)	7,831 (±123)	9,414 (±186)

The F-test, a statistical means of determining whether standard deviations of data sets are statistically different at a given confidence interval, was performed and revealed that at the 95% confidence level, there were no significant differences. The 95% confidence interval was used for this test, as it was for all statistical tests in this study unless otherwise noted. Means were compared by applying the t-test from which determination was made as to whether two means could be considered to come from the same population within the 95% confidence interval.

The effects of fiber tension on material properties were evaluated by comparing test results from stock fabricated at the same die temperature profiles and line speeds, but different tensions. Thus cases 1, 2, and 5 were compared to one another as were cases 3 and 6 and 4 and 7.

Results of the t-test on flexure modulus data indicated that only cases 3 and 6 were significantly different at the 95% confidence level. At the 99% confidence level differentiation between cases 3 and 6 required additional experiemental data. Similar results were obtained for the short beam shear data. Meaningful differences in values of maximum shear stress were found between cases 4 and 7. Analysis of maximum flexure stress yielded ambiguous results. Cases 2 and 5 were shown to have significant differences in values of maximum flexure stress at the 95% confidence level, but at the 99% level the indication was a need for more data. Identical results were obtained for comparison of cases 3 and 6.

These three comparisons show that improved mechanical properties, when they occurred, were correlated to increases in tow tension from zero to half. This indicates that at these tension levels pulling force is of minimal importance as a processing parameter except in terms of machine operation.

A second set of comparisons was made using samples produced under different die temperature set points but the same tension and line speed. Thus, t-tests were applied between cases 2 and 3 and between cases 5 and 6.

The flexure data for these runs yielded mixed results. The t-tests showed no significant differences between flexure moduli of cases 2 and 3. In contrast, flexure moduli for cases 5 and 6 were found to differ statistically. The t-tests for differences in maximum flexure stress, revealed no differences between cases 2 and 3 or cases 5 and 6. Definite differences were identified in values of maximum shear stress between cases 2 and 3. The t-test results comparing maximum shear stress values for cases 5 and 6 were inconclusive.

This set of comparisons showed that for all properties examined, flexure modulus, maximum flexure stress and maximum shear stress, better results were obtained when the stock was produced with set points of 350°F rather than 330°F.

Finally, a third set of comparisons was made between samples produced with different line speeds and the same tension and die temperature set points. Test results for case 3 were compared to those for case 4, and results for case 6 were compared to those for case 7.

Maximum shear stresses of cases 3 and 4, as well as cases 6 and 7 were shown to be statistically different. Cases 3 and 4 were also found to have statistically different flexure moduli while those of cases 6 and 7 did not. Values of maximum flexure stress for cases 3 and 4 and cases 6 and 7 did not differ significantly.

In all instances, save one, the lower line speed produced a composite with better material properties. The single exception was the stock produced with zero tension and a die profile of 350°F in which case the stock produced at the higher line speed exhibited a greater maximum flexure stress.

One might assume, a priori, that increased tension during processing would increase the packing density of the fibers, and, thereby, decrease the fiber surface area accessible to the resin for wet-out. Observations made during runs appear to support this conclusion since the amount of resin collected at the last preformer under conditions of higher tension was less than the amount collected during previous runs at lower tensions. Results of burnout tests, however, contradicted these observations.

Results of burnout tests together with densities are reported in Table 3. These are average values and all except one are based on results from four samples. Values from the case of zero tension, 9 inches/minute and a 350°F temperature profile was based on two samples.

Table 3. RESIN BURNOUT AND DENSITY DATA

Resin (wt%)	Density (g/cc)	Tension	Temp. (°F)	Line Speed (in./min)
21.7	2.06	Full	330	6
21.4	2.04	Half	330	6
19.7	2.10	Half	350	6
20.4	2.07	Half	350	9
20.0	2.10	None	330	6
18.5	2.07	None	350	6
21.6	2.02	None	350	9

The maximum difference in resin weight percent was only 3.2%, corresponding to a density difference of approximately 1.5%. The calculated resin weight percent for all samples had a mean value of 20.5% and a standard deviation of ± 1.18 while density averaged 2.06 cc with a standard deviation of ± 0.03.. Thus, there was no significant difference in resin content, probably a consequence of the efficiency of the resin bath rollers and preformers in saturating the fiber mass with resin.

To conclude, in terms of both the flexure modulus and short beam shear tests two samples proved superior. These samples contained the slightly higher fiber volumes but more importantly both were produced at 6 inches per minute and a 350°F die temperature profile. Aside from this observation perhaps the most noteworthy aspect of the data was that neither density, tension, nor percent weight resin appears to be correlated to any specific trend involving flexure or shear strength.

Viscosity

Although Schott et al., found no effects for epoxy pultrusions due to viscosity, verification of the applicability of their results to the process described in this paper are required due to dissimilarities in experimental conditions. The experiments described within this report were performed on an industrial scale, whereas the experiments performed by Schott et al. were on a laboratory scale. Additionally, the resin system formulation used in the two processes differ. This investigation's resin system included an internal release agent and the viscosity modifying filler Zeothix, in addition to the components used in Schott's process. In terms of fiber volume the ratio of the land length to area of the laboratory scaled preformer die is closer to that of the heated pultrusion die as opposed to the preformers. Another possible source of disparity stems from the use of rollers in the actual pultrusion runs which squeeze the fiber/resin mass facilitating fiber wet-out and removing excess resin.

Eight-hour viscosity experiments were carried out on the complete resin system formulation to establish a baseline. The results showed only slight increases in viscosity during the tests, however, observations made during the actual pultrusion runs indicated that there were greater viscosity changes in the resin bath than those experienced in the laboratory beakers.

To determine the effect that changes in the resin bath viscosity have on the anhydride cured system during a typical pultrusion run, viscosity was monitored for a five-hour run. Experiments were conducted at a line speed of nine inches/minute and a die temperature set point of 350°F. Because previous experience had shown that excessive air bubbles within the resin affect viscosity readings, just-mixed resin was allowed to rest for 1.5 hours before processing. Measurements were made at intervals throughout the run. For each measurement, approximately 400 milliliters of resin was removed from the bath and tested with a Brookfield® viscometer. A record of the time of each refill of the bath was also made. Since the line speed was known and was constant, the viscosity of the resin for all samples could be calculated.

Figure 2 compares the results of viscosity measurements for resin in the pultruder bath during processing, and resin in a beaker. At the end of five hours running time the resin bath viscosity was nearly twice that measured in the laboratory beaker (4000 centipoise to 2300 centipoise). While the reasons for these differences were not determined it is theorized that the increase in viscosity was due to the accumulation during processing of dissolved sizing and/or broken fibrils in the bath.

Results from the various tests characterizing the stock pultruded in the experiment described above are shown in Table 4. No relationship between the density of the stock and the resin bath viscosity is indicated. Nor does it appear that resin weight percent is dependent on the viscosity of the resin system.

This evidence, however, does not exclude the possibility of viscosity effects, since the distribution of resin within the fiber bundle may still be affected.

Maximum shear stress, maximum flexure stress and the flex modulus exhibited no correlation to density or resin weight percent. However, some trends are evident in the plots of maximum shear stress, maximum flexure stress and flexure modulus as a function of the resin viscosity, Figure 3, 4, and 5, respectively.

Table 4. EXPERIMENTAL DATA PERTAINING TO RESIN BATH VISCOSITY

Bath Visc (cP)	Density (g/cc)	Resin (wt%)	Max. Shear Stress (psi)	Flex Modulus (ksi)	Max. Flex Stress (psi)
2155	2.02	21.6	9414 (±186)	7831 (±123)	177,085 (±5103)
2180	2.04	21.2	9328 (±110)	8033 (±125)	183,536 (±3539)
2343	2.11	21.4	9525 (±125)	7951 (±189)	181,185 (±5184)
2337	2.00	21.7	9340 (±136)	8007 (±161)	177,787 (±4197)
2512	[illegible]	21.4	9385 (±192)	8023 (±153)	178,626 (±4419)
2530	2.00	21.6	9239 (±323)	8017 (±75)	179,459 (±3888)
2561	2.03	22.4	9595 (±225)	7981 (±133)	179,111 (±3964)
2718	2.06	21.9	9471 (±168)	8079 (±138)	181,379 (±1969)
3011	2.00	21.6	9564 (±190)	8074 (±179)	179,013 (±3591)
3324	2.05	21.4	9581 (±241)	7982 (±136)	178,555 (±5270)
3755	2.03	21.5	9343 (±176)	7883 (±144)	173,946 (±4074)
3999	2.01	21.6	9605 (±183)	7694 (±70)	175,310 (±10,830)

The largest difference in maximum shear stress between any two samples is 396 psi. This difference occurs between samples produced from resin at 3999 cP and 2530 cP and corresponds to a change of only 4.3%. The insignificance of this change, is underscored by the fact that the standard deviation of the maximum shear stress value at 3999 cP is ± 323 psi. There does, however seem to be a trend , as shown in Figure 3, in which increasing resin viscosity correlates to increasing values of maximum shear stress. This trend, though, is slight and requires additional supporting data for confirmation.

Figure 4 is a plot of the maximum flexure stress as a function of viscosity and appears to show a trend of decreasing maximum flexure stress with increasing viscosity. The maximum difference in flexure stress occurs between samples made from resin at 3755 cP and 2180 cP. This difference is 9590 psi and represents a 5.5% change in maximum flexure stress.

Figure 5 is a similar plot for flexure modulus. It illustrates a trend which appears parabolic over the viscosity range examined. Examination of the data reveals a maximum difference of 385 ksi between values for the highest, 8079 ± 138 ksi and the lowest, 7694 ± 70 ksi, flex moduli, a change of only 5%.

Comparing populations of flexure modulus mean values, using the t-test at a 99% confidence level, offers additional information. The greatest value of the flex modulus occurs for samples made from resin at 2718 cP while the lowest values are for samples made from resin at 2155 cP and 3999 cP, the lowest and highest resin bath viscosities. The average modulus of samples made from the lowest viscosity resin fall into the same population as those samples having the highest value of flex modulus. The samples with the highest viscosity are not from the same population.

The results from this set of experiments agree with the findings of Schott et al. (see Reference 6) in that the resin content was independent of viscosity. Other indications were that an increase in resin bath viscosity tends to slightly increase maximum shear strength but also slightly decreases maximum flexure stress. A range in bath viscosity from about 2700 to 3000 cP resulted in a product with a maximum flexure modulus, as well as very good maximum flexure and shear strengths. These indications, however, are based on changes of 5.5% or less and are therefore suspect. Thus, for this particular resin system it may be assumed that increases in the bath viscosity over a normal operating shift do not alter the mechanical properties of the stock.

Die Temperature and Line Speed

Unlike polyesters which requires an impulse of energy to cure, an epoxy requires a period of sustained heat. In pultrusion the amount of heat transferred into the composite is dependent on both the line speed and die temperature. Reduction in die residence time may be achieved by raising the die temperature although this will produce higher gradients of both temperature and composite cure. Lower die temperatures, however, require a longer residence time. Thus, there exists a window within which consistently good stock may be pultruded. This window may be characterized in part by the position of the gel zone in the die. In the case of polyester resins the gel point precedes the exotherm whereas, in epoxies, gelation generally occurs after the maximum exotherm temperature and usually lacks a definitive point. In either case the position of peak exotherm temperature remains a convenient indication of the approximate position of the gel zone in the die.

In order to determine whether this indicator can be related to product quality a series of experiments were undertaken. The pultruder was set up as for the tension and viscosity experiments but with a different fiber dispensing system. E glass was rewound on plastic spools, and mounted in rows, three across, in the creels. This configuration supplied sufficient drag to satisfactorily tension and align the tows thereby, eliminating the need for the introduction of additional tension through tensioning tubes.

Peak exotherm temperatures were recorded as the pultruder was run at line speeds of 6, 9, and 12 inches per minute and with die temperatures between 330 and 370 degrees Fahrenheit at 10 degree increments. The temperatrue profile along the die length was kept flat; that is, the same control temperature was maintained in all three zones. It was felt that these increments would provide discernible changes in the rate of cure and heat released thereby producing observable decreases in the cure times.

Table 5 lists the average resin weight percent and density of the stock produced under the designated conditions. The average weight percent of resin for all specimens (40) was 20.8% with a standard deviation of 0.974. This correlates to a fiber volume fraction of 64.5%. The average density for all the samples examined here was 2.10 g/cc with a standard deviation of ± 0.058 g/cc.

Table 5. DENSITY AND WEIGHT PERCENT DATA

Temp. (°F)	Line Speed (in./min)	Density (g/cc)	Resin (wt%)
330	6	2.08	19.5
	9	2.08	21.1
	12	2.08	22.1
340	6	2.08	20.4
	9	2.16	20.9
	12	2.09	21.2
350	6	2.09	20.4
	9	2.06	19.9
	12	2.05	21.8
360	6	2.07	21.7
	9	2.09	22.2
	12	2.10	20.6
370	6	2.06	20.0
	9	2.15	20.7
	12	2.15	20.5

An approximation of the void content of the composite stock was made using the ASTM standard method (D 2734-76). Basically this method uses the resin burnout data to calculate a theoretical density which is then compared to a measure density. The assumption is that the density of the resin in the composite is the same as that of a neat resin casting. This is not strictly correct since differences in curing (heat and pressure, for example) and the chemistry and molecular forces contributed by the reinforcement alter the neat resin density. This alteration can cause the calculation of a void content to be lower than it actually is, sometimes even producing negative results. Another problem associated with this calculation and of concern in this application, is the addition to the resin of fillers and an internal mold release which may also change the density of the cured system

The void content of a composite is considered significant because it is believed to have an effect on mechanical properties since voids in the matrix could inhibit load transfer from the matrix to the fibers. Increased void content increases the composite's susceptibility to water penetration and, therefore weathering, and because of random distribution voids also produce increased scatter in strength properties.

The calculations used to produce the data found in Table 6 do not account for the addition of mold release or silica filler to the resin. It was assumed that the composition of the resin system for all the studies was the same and that any error incurred due to the filler or mold release would be equal across the board. Consequently, the values in Table 6 are not so much accurate representations of the void content as they are relative values for the evaluation of processing parameters. Comparison of values in Table 6 clearly show that, with the exception of one value, a line speed of 6 inches/minute consistently produced composite stock with a lower void content. In terms of die temperature set point the average values of void content point to an optimum die control temperature of 350°F.

Table 6. VOID CONTENT CALCULATIONS

Line Speed (in./min)	Die Control Temperature (°F)					Avg.
	330	340	350	360	370	
6	0.56	0.25	0.73	0.93	1.07	0.71
9	0.88	4.57	1.16	2.36	3.90	2.56
12	1.78	1.46	0.05	1.40	3.72	1.68
Avg.	1.07	2.09	0.65	1.56	2.90	

Table 7 displays the results of the short beam shear tests. In general, the maximum shear stress results show that for a given die temperature set point an increase in the line speed produces a decrease in the shear stress values.

Table 7. MAXIMUM SHEAR STRESS DATA (psi)

Temp. (°F)	Line Speed (inches/minute) 6	9	12	Avg. Based on Temp.
330	10147 (±281)	9963 (±286)	9624 (±185)	9912 (±333)
340	10181 (±319)	10130 (±238)	9894 (±167)	10045 (±279)
350	10283 (±284)	9993 (±268)	10095 (±305)	10132 (±310)
360	10177 (±414)	9795 (±280)	9604 (±319)	9948 (±442)
370	9864 (±243)	9801 (±285)	9356 (±208)	9668 (±334)
Avg. Based on Line Speed	10130 (±341)	9956 (±304)	9681 (±331)	

Figure 6 is a plot of shear stress versus die temperature set points as a function of line speed. In it, peak values of maximum shear stress for a particular line speed were found to exist at a particular die temperature set point. For line speeds of 6 and 12 inches per minute this peak value was obtained at a die temperature set point of 350°F. At a line speed of 9 inches per minute the peak value is observed at a temperature of 340°F. However, the stress values are similar for stock produced both at 350°F and 340°F. This tends to indicate that for this particular resin system optimum operating conditions exist at a die set temperature of 350°F.

Table 8 presents results of the flexure tests. The absence of flexure data for the stock produced at 9 inches/minute is due to lack of sufficient material quantities. This deficit is moderated by the amount of other data and the fact that flexure data was collected for the runs made at 6 and 12 inches/minute, the extremes in line speed.

A plot of the average of maximum shear stress for all line speeds versus die temperature set point is presented in Figure 7. This data also points to the die set point of 350°F as that which produces the best short beam shear results.

Table 8. FLEXURE DATA

Temp. (°F)	Line Speed (in./min)	Max. Flex Stress (psi)	Flex Modulus (ksi)
330	6	186,082 (±3759)	6831 (±82)
340	6	180,411 (±4331)	6755 (±73)
350	6	181,705 (±3919)	6740 (±122)
360	6	181,246 (±2908)	6840 (±148)
370	6	184,109 (±3414)	6826 (±90)
330	12	175,845 (±2526)	6650 (±123)
340	12	176,079 (±4604)	6725 (±91)
350	12	178,851 (±2006)	6675 (±104)
360	12	185,783 (±3748)	6780 (±102)
370	12	182,498 (±4625)	6817 (±65)

In general, the values of maximum flexure stress and flexure modulus were not strongly affected by the operating conditions utilized. The largest difference in maximum flexure stresses is 926.5 psi, or a change of about 9.9%.

Figure 8, a plot of the maximum flexure stress versus the die temperature set point with line speed as a parameter, offers somewhat different results. For the most part, the stock produced at 6 inches/minute has higher values for flexure stress than that produced at 12 inches/minute. The exception is for stock produced at a die temperature set point of 360°F, in which case the stock fabricated at a line speed of 12 inches/minute has a higher value. The greatest difference in maximum flexural stress, 10,237 psi, was noted at a die temperature of 330°F and represents a difference of 5.8%, between values obtained for the two line speeds.

These results are echoed in Figure 9 which is a plot of the flexure modulus versus die temperature set point with line speed as a parameter. In this case there are no inconsistencies in the dominance of the modulus of stock fabricated at the lower line speed. The largest difference between two averages occurs again at the 330°F die temperature set point but this only represents about a 2.5% difference. The minor difference existing between any two averages in the flexure data is probably due to the fact that the modulus of the composite is fiber dominated. These slight variations may be due to dissimilarities in the manner in which the load is transferred to the fibers, possibly a result in variations of cure characteristics.

One cure characteristic is the crosslink density, a measure of which can be provided by the glass transition temperature, T_g. The glass transition is considered a second-order transition since it invloves a discontinuous change in a thermodynamic property such as specific heat. A differential scanning calorimeter (DSC), dynamic mechanical analyzer (DMA), or thermal mechanical analyzer (TMA) is usually used to determine the T_g of a material. In this study the T_g of the pultruded stock was determined using a Perkin-Elmer DSC-2. The DSC is well suited for this task since its trace is actually a continuous plot of the specific heat as a function of temperature.

The T_g tests were conducted under nitrogen at a rate of 10°C per minute over the range of 20°C to 230°C. After the first sweep, the sample was quickly cooled and a second sweep was made to determine the glass transition temperature after thermal exposure. The initial scan is made to relieve possible residual stresses and to insure completion of the cure. It is important to note that the values determined for T_g are method dependent, most likely due to time-stress conditions of the test. It should also be noted that the sample size is very small and perhaps is not truly representative of one actual fiber/resin ratio of the pultruded stock. This being the case, T_gs presented in this study do not necessarily represent the ultimate glass transition temperature but do provide relative values for comparison, and identifying trends.

The results of these tests are presented in Table 8. Initial DSC scans produced some curing reaction after the first glass transition peak in all tests. The residual heat of reaction data reinforces previous evidence that the 350°F die temperature set point offers the best cure environment for this resin system. Stock cured at this temperature and a line speed of 6 inches/minute is by far the most completely cured stock. Each line speed, stock produced at 350°F is more completely cured than that produced at 330°F. At a line speed of 6 inches/minute it is also more completely cured than stock produced at 370°F, while at line speeds of 9 and 12 inches/minute the cure is comparable.

Figure 10 is a plot of the two glass transition temperatures for each line speed as a function of die temperature. It can be seen that the T_g from the first sweep is a function of die temperature, its value decreasing as the die temperature profile is increased. Overall the 6 inches/minute stock produced at higher temperatures had the lowest glass transition temperatures, while the 9 inches/minute stock offered the highest. The best results were obtained at 330°F with a line speed of 6 inches/minute. The difference between the highest and lowest T_g is about 8°C.

In Figure 10, the upper portion of the plot shows the results of the second sweep. There is an average increase of about 23°C in the T_g for all samples. The higher line speeds do consistently produce somewhat higher T_gs although differences among stock produced at the same die temperatures are rather insignifcant. As in the first sweep, the relationship between die temperature and T_g is still prevalent. The difference between the first and second T_g is not readily explained by the residual heat of reaction and therefore could in part be due to the relief of residual stresses.

Analysis of the Exotherm Data

While certain properties of the composites produced in this study can be attributed to the presence, type and dominance of fiber reinforcement, a portion is also dependent upon the structure of the matrix, since its purpose is to transfer the load to the reinforcement. This structure is determined by the chemistry of the curing reaction and, therefore, is defined on the molecular level. In the case of the thermosetting resin used here this structure is described by the crosslink density. The mechanical tests described previously provided some evidence as to which conditions induced the most thorough crosslinking, most notably a die temperature set of 350°F.

Another aspect of the cure analysis involves the examination of effects associated with the curing exotherm. Strictly speaking the exotherm is the liberation of heat energy during the chemical reaction which is intrinsic to the curing process. It has been observed that the rate of the exotherm has an effect upon the product's surface quality, with adverse quality resulting from spalling and sloughing. If an exotherm proceeds too rapidly, the heating can become uneven and uncontrolled and is believed to produce voids or internal cracking. This latter effect probably results from the release of residual stresses caused in part by large thermal gradients experienced in processing. The rate of exotherm also plays a part in the degree of cure. A detrimental effect is reduced crosslink density resulting from the degree of cure proceeding such that viscosity effects immobilize the system before all the epoxy groups are consumed. Finally, it is also possible that the exotherm might reach temperatures high enough for thermal degradation of the composite matrix thereby having negative effects on the resultant product's physical properties.

For the ensuing studies information was obtained from temperature versus time curves recorded during processing. The data for the curves were acquired by imbedding thermocouples into the moving fiber/resin mass prior to its entry into the die.

The relative importance of the thermal processing history, with respect to final properties, is underscored by a reexamination of the results of the tension and viscosity experiments. Insofar as the tension experiments were concerned the physical test results indicated that neither induced fiber tension, density nor resin weight percent seemed to correlate to any specific trends in product strength. Instead the data demonstrated that the material processed at a specific temperature and line speed (350°F and 6 inches/minute) exhibited better properties.

The effect of tension on properties is mirrored in its effect on thermal histories. At a 330°F die temperature profile and a line speed of 6 inches/minute material was processed at each of the three tensions. Thermocouple locations (from the top surface) for these examinations were 0.077 inches for full tension, 0.074 for half, and 0.083 for the zero tension case. All were approximately centrally located in the width dimension. The peak exotherm temperatures were 362°F, 358°F, and 361°F for the full, half, and zero tensions, respectively and occurred along the die at positions of 18.4, 18.0, and 18.6 inches. The temperature histories are very similar with the minor variations possibly due to variations in thermocouple locations. Since the exotherm is a function of the mass of resin present, these results are consistent with the resin weight percents in their similarity. Material fabricated at 6 inches/minute and 350°F

for half and zero tension shows maximum exotherm temperatures of 376°F and 383°F, at die positions of 16.9 and 16.2 inches, respectively. The somewhat larger differences between these values may be related to larger differences in thermocouple locations (depths of 0.060 and 0.082 inches). The relevant point is that materials produced under the same fiber tension and line speed, but different die temperature profiles had significant differences in shear and flexural strength while those produced at the same line speed and temperature, but different tensions had similar shear and flexure strengths. These differences/similarites are reflected in the maximum exotherm temperature and position.

In the case of the viscosity experiments there was no evidence of a relationship between increasing resin bath viscosity and the resultant material's mechanical properties. This too is reflected in the thermal histories of stock pultruded near the viscous extremes, which are illustrated in Figure 11. The two curves represent the thermal histories of stock produced with resin bath viscosities of 2337 and 3999 centipoise. The depth of the thermocouples was 0.110 and 0.116 inches, respectively and the most outstanding aspect of the curves is their similarity. The locations of the maximum exotherm temperatures are virtually the same. The magnitude of the peak temperatures at about 376°F are not only identical but equal to the maximum temperature achieved at a similar depth in samples processed at the same temperature and line speed but with increased fiber tension.

This same analysis may be applied to the die temperature and line speed experiments. The largest differences in mechanical testing were observed in the short beam shear results. The best results were consistently obtained from a combination of the 350°F and 340°F settings followed by those at 330°F. The results at 370°F were consistently poorer than any of the other settings. This die temperature dependence can be translated to a die profile dependence in order to produce stock with optimum properties.

The most complete set of data was collected at depths of 0.060 to 0.070 inches from the stock surface, and shows that the optimum short beam shear results were obtained when the maximum exotherm temperature was between 360°F and 370°F. Equally important, this maximum temperature was obtained at a time between 1.7 to 2 minutes after entry into the die. The actual center line temperature would be several degrees higher than those measured, ranging from 365°F to 375°F or approximately 25° above the die profile. This rise is, of course, resin system dependent and is in keeping with the observations of Outwater's investigations[9] involving polyester resins.

A more detailed examination of these obseravations is made from the thermal history plots. Figure 12 is a time-temperature plot representative of that stock produced at a line speed of 6 inches/minute and a 350°F profile. The curve is approximated by two intersecting lines of fit to adjacent portion of the curve. The first segment roughly corresponds to the portion of the curve in which conduction from the die is the dominant mode of heat transfer. In the second segment, the exotherm becomes a factor. The analysis proceeds from the realization that the optimum temperature excursion and its location along the die may be represented by the second section of the curve. If this portion of the curve is treated as a striaght line, the maximum temperature may be represented by the slope.

Each time-temperature curve was divided into the two segments described and a straight line was fit to the section associated with the exotherm. The slopes of these lines were then grouped according to thermocouple location in the composite (in the thickness direction), die temperature, and line speed. The optimum line speed and temperature were identified by characterizing the material.

No single set of conditions produced stock which had both the best short beam shear and flexural results. In fact, more often than not, samples exhibiting the highest flexure modulus posted poor results in short beam shear testing. For each group of line speed and temperature settings, the sample offering the best combination of results for short beam shear, flexure stress, and flexural modulus was chosen as

9. OUTWATER, J. O. On the Mechanics of Pultrusion, The 41st Annual Technical Conference, RP/CI, Society of the Plastics Industry, January 1986.

optimum. This new group was then examined in terms of the slopes of the fitted lines and a range of optimum slopes obtained. At a depth of 0.060 inches the range was between 0.060 to 0.7 and for the center line it was 0.7 to 0.9. This range corresponded to die temperature set points of between 340°F and 350°F. The samples produced at these temperatures, regardless of the line speed, also exhibited the lowest void contents and the least amount of residual heats of reaction. They also proved to be the best candidates through a more subjective means of testing, that of the visual inspection of surface quality. The stock produced at these temperatures had a smooth glossy surface. Stock produced at different settings, especially that at the highest temperature, were marked by sloughing and a rough surface often containing glass splinters as opposed to a smoother resin rich surface.

Finally, one other way to interpret the information offered by these plots is to measure the area under the curve. This integration can be thought of as representing the sum of the heat energy put into and released by (the exotherm) the system. The integration was carried out from die entrance to exit over the various temperature profiles and line speeds examined. While there was no discernible trend upon cursory observation of the data, a plot of the integrations of the curves from the samples offering the best mechanical test results versus die dwell or residence time, gave interesting results (short beam shear tests). These points were well fit by a line with the equation $Y = 299.3X - 258.8$ where Y is in °F-min (the units of the integration) and X is the dwell time in minutes. The line of fit had a correlation coefficient of 0.999. The plot is illustrated in Figure 13. The second set of data points on the plot correspond to a similar analysis for a group of samples that produced much lower mechanical test results (short beam shear test). The fact that this line is above that based on the best results supports the hypothesis that thermal degradation might have been a factor in some cases. While this does not offer a great deal of insight into the process per se, a plot of this nature may be able to serve as a means of estimating optimum conditions for pultruding this reinforcement/resin system.

CONCLUSIONS

The results from the tension experiments indicated that there was no significant gain in mechanical properties with increased tension. Consequently, this downplays the role fiber tension has as a processing parameter. Experience has shown, however, that a threshold tension in the creels is required to collimate the tows as they move through the process, thus, avoiding intermingling or snagging in the die aiding in the mechanics of processing. The appropriate tension appears to be that which simplifies both start-up and processing operations. Additional pulling requirements were easily met by the machine, although it should be noted that this force is also dependent upon the number of tows and cross section profile used.

The profile of the stock used in this study was simple in geometry, and therefore, tow tension might be less important in this case than in a part with a more complex cross section. Toward this end a similar effort should be extended toward examination of the effect of selective tow tension in more complicated cross sections.

This particular resin system is very forgiving in terms of resin bath viscosity. There was some indication that a range in bath viscosity from 2700 to 3000 cP produced a product with a maximum flexure modulus and that increasing bath viscosity produced a product with increased shear stress values. Measurements of the resin viscosity made during processing revealed that moving tows through the resin appeared to greatly increase bath viscosity, an effect which was not produced in the laboratory testing of the resin system alone. The process was able to accomodate a near twofold increase in resin bath viscosity during the course of a five-hour pultrusion run producing changes in the product's mechanical properties of 5% to 6%. The results confirmed previous studies in finding that the resin content of the pultruded stock was independent of the resin bath viscosity from which it was produced.

Viscosity effects are system dependent and so each resin system must be analyzed individually to determine the effect, if any, that resin bath viscosity might have on the final mechanical properties of the composite stock. Since viscosity is relatively easy to monitor and modify (by adding fresh resin) on line, it merits further investigation as a control parameter for the process.

The studies involvng the die temperature profile and line speed suggests that there is an optimum combination of line speed and die temperature such that consistently good stock is pultruded; however, small deviations from the optimum conditions result in relatively minor variations in mechanical properties. Increases in line speed at a given die temperature profile were shown to result in a decrease in the mechanical response of the composite, but the differences are small enough to insure an acceptable product at higher pultrusion rates. A die control temperature of 350°F proved to be an optimum temperature for a variety of line speeds studied.

Finally, the real-time temperature histories collected while running the pultruder over a large range of operating conditions provided a set of optimum parameters for the consistent production of quality stock. This effort showed that there was an optimum temperature excursion of about 25°F which should occur at a time between 1.7 and 2 minutes after entry into this particular die. This was echoed through the determination of a series of depth dependent time-temperature slopes which were correlated to the optimum product properties.

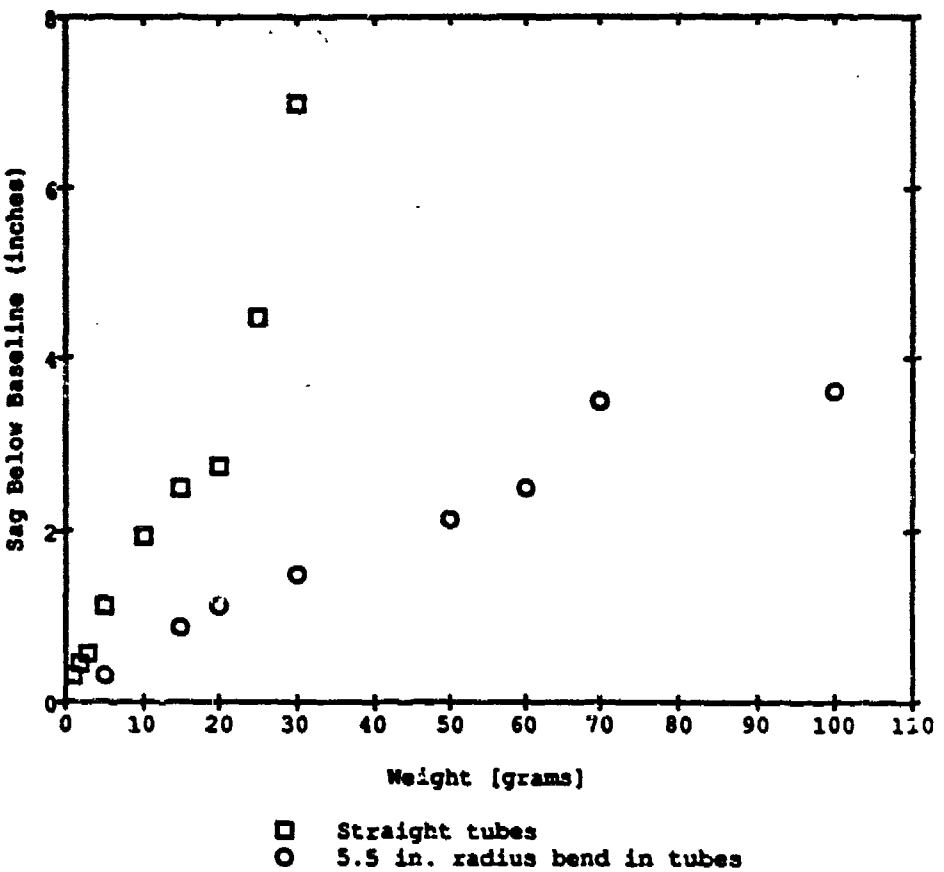

Figure 1. Static fiber tension for straight tubes and tubes with a 5.5-inch bend.

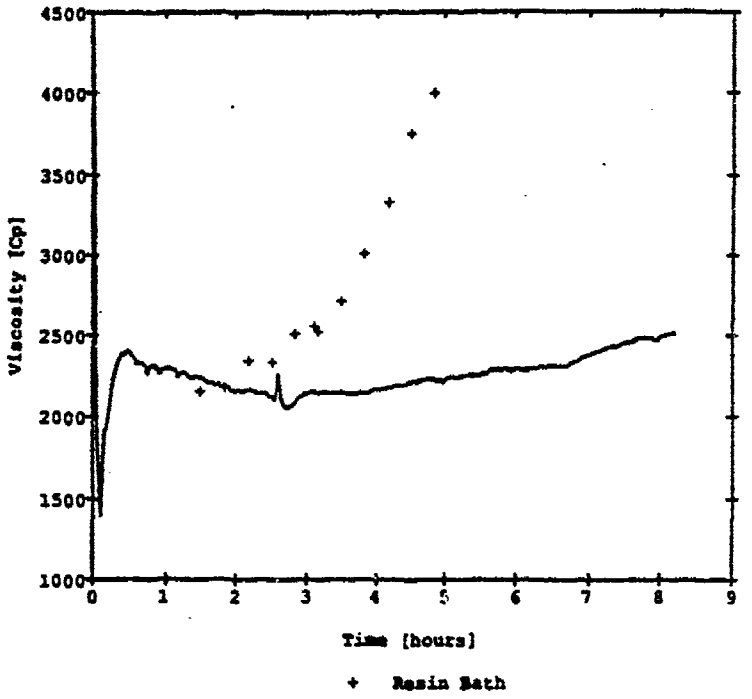

Figure 2. Effect of moving tow through resin bath where base curve represents the laboratory sample minus the effect of the glass.

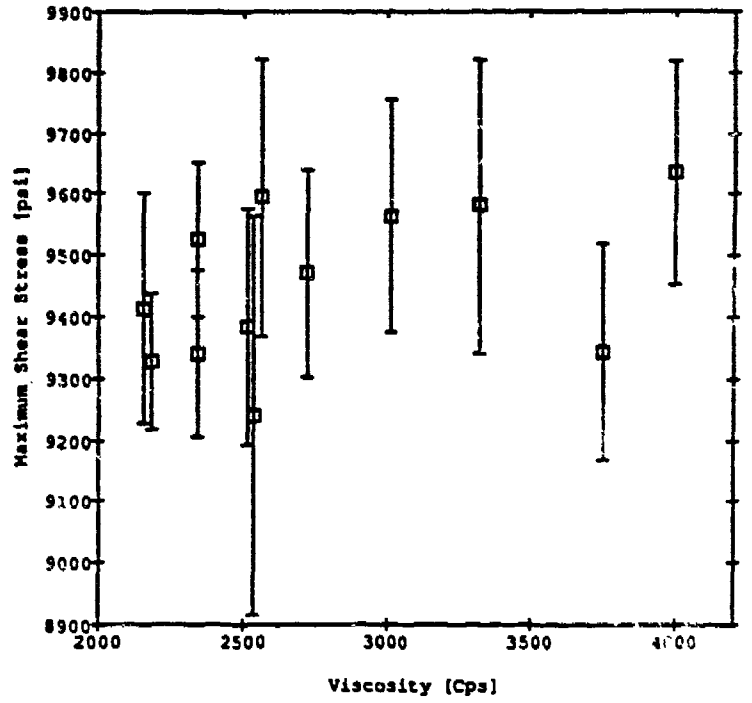

Figure 3. Plot of the maximum shear stress as a function of resin bath viscosity.

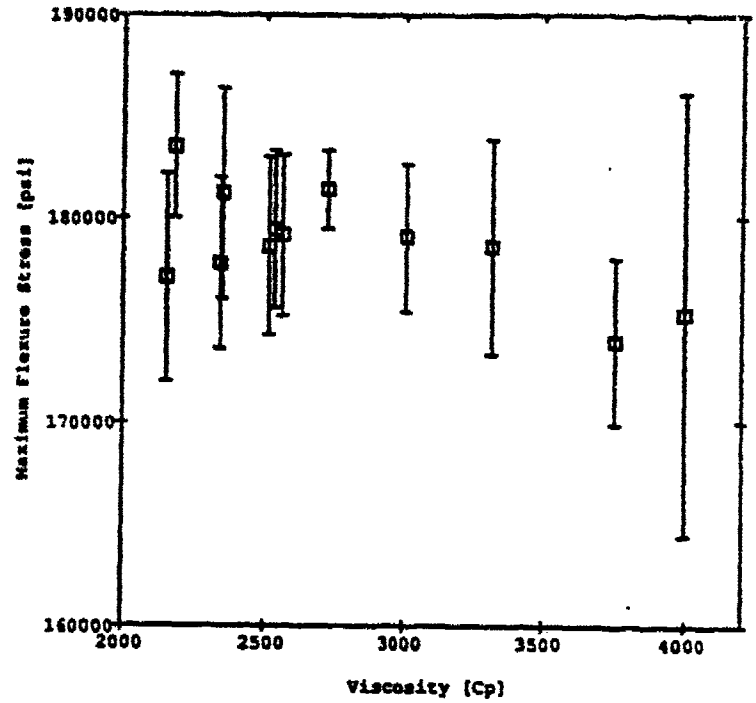

Figure 4. Plot of the maximum flexure stress as a function of resin bath viscosity.

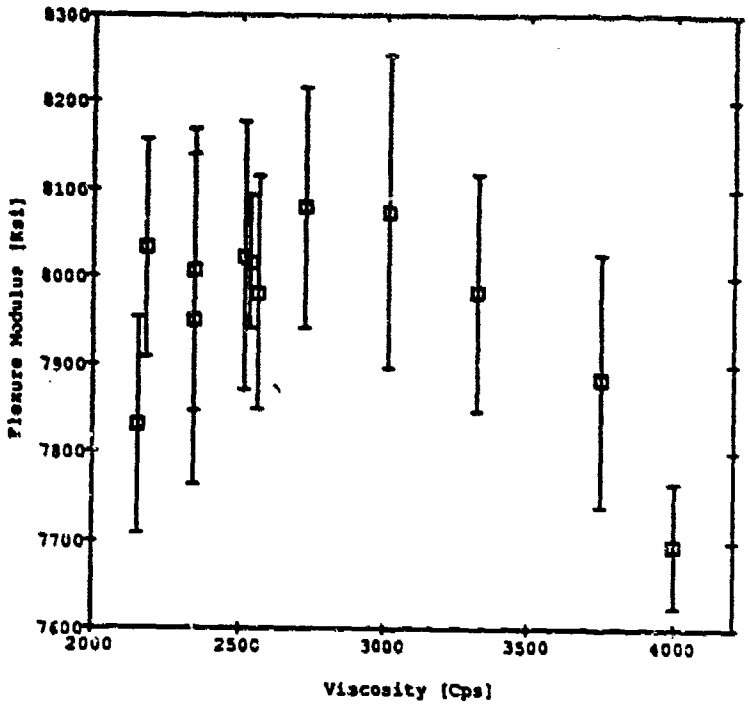

Figure 5. Plot of the flexure modulus a function of resin bath viscosity.

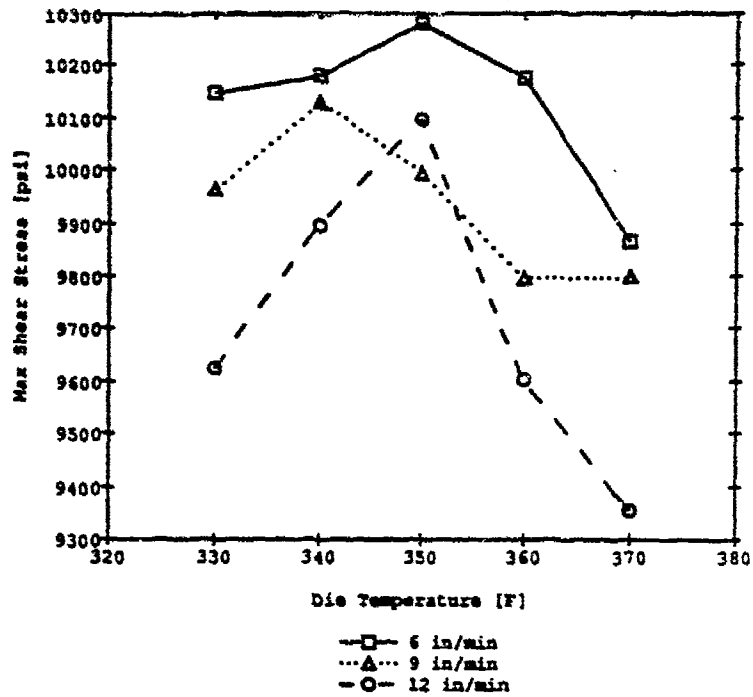

Figure 6. Plot of maximum shear stress versus temperature profiles as a function of line speed.

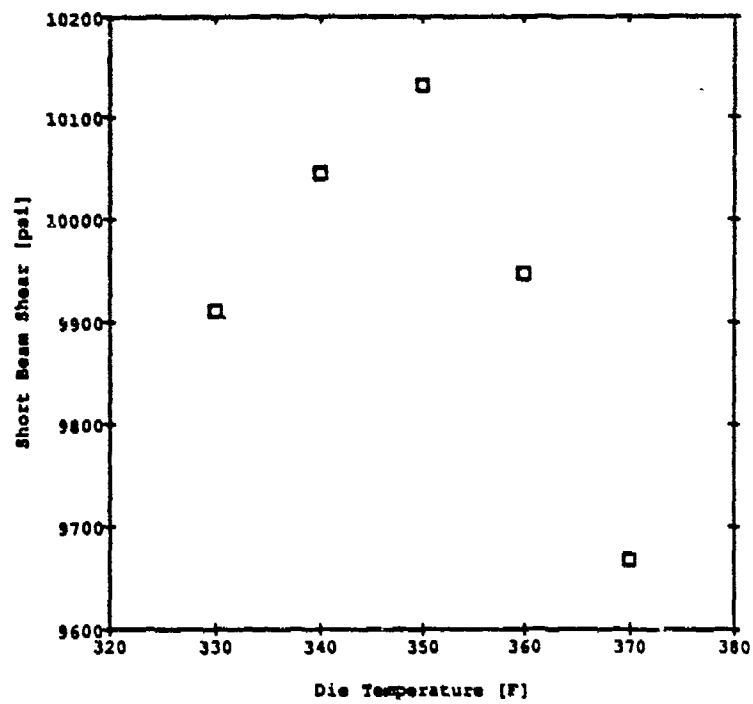

Figure 7. Average short beam shear data as it pertains to die temperature profile.

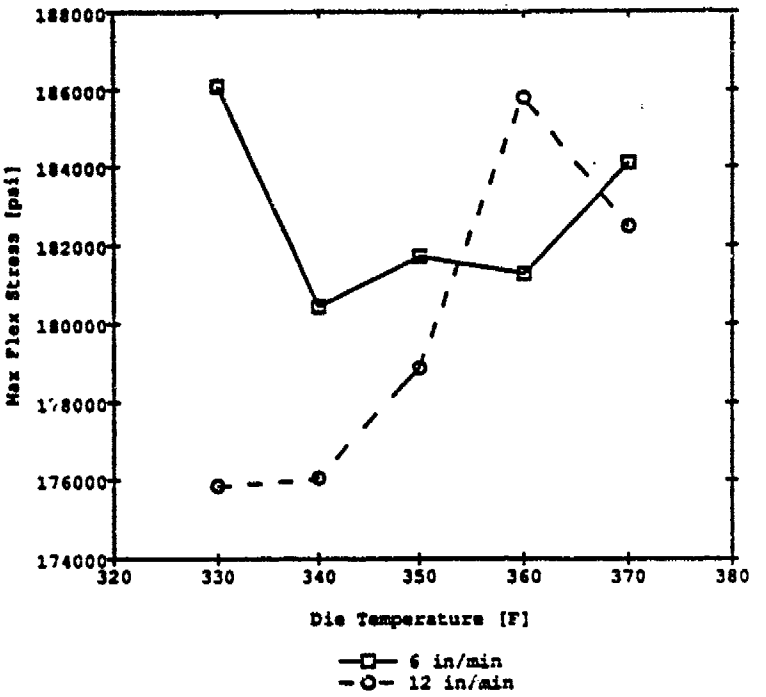

Figure 8. Maximum flexure stress data versus temperature profiles as a function of line speed.

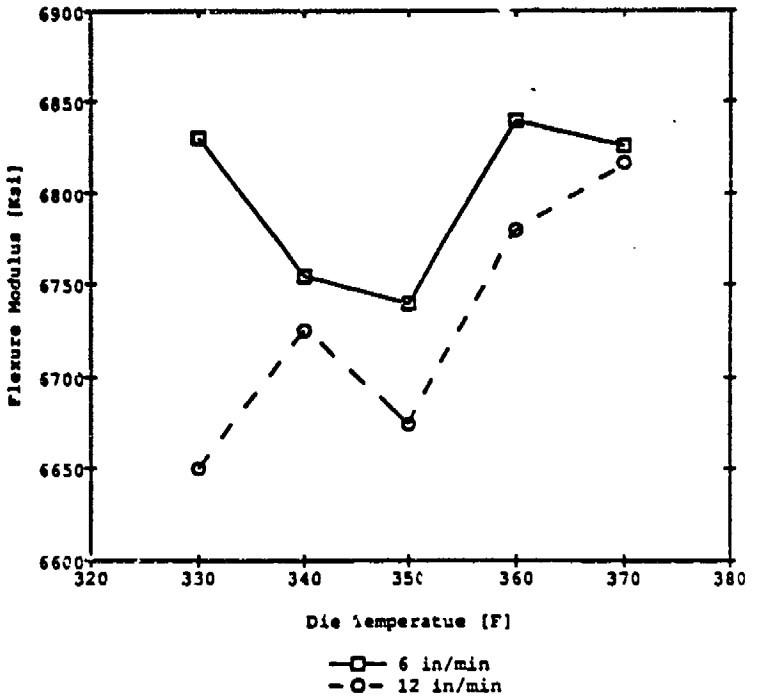

Figure 9. Flexure modulus versus temperature profiles as a function of line speed.

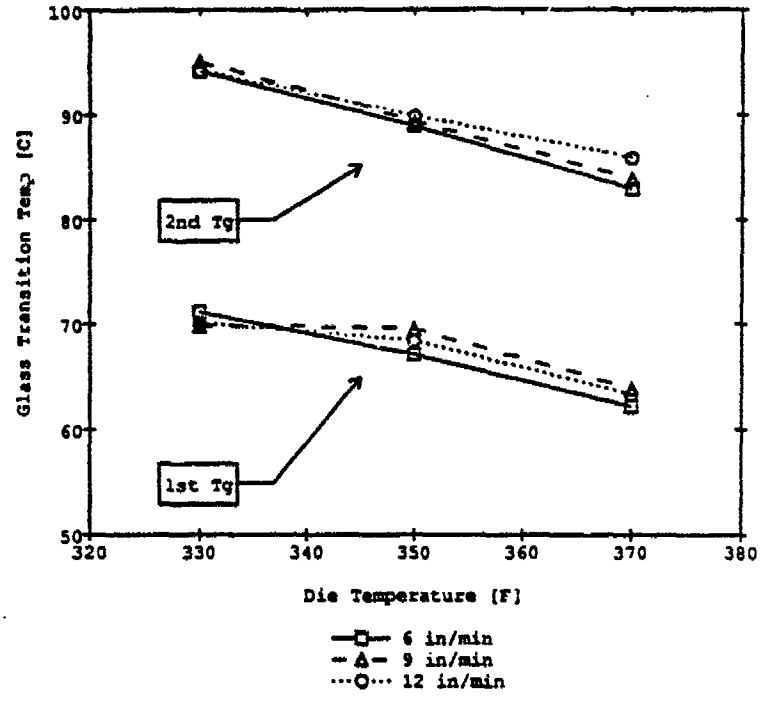

Figure 10. First and second T_gs versus die temperature profile as denoted by line speed.

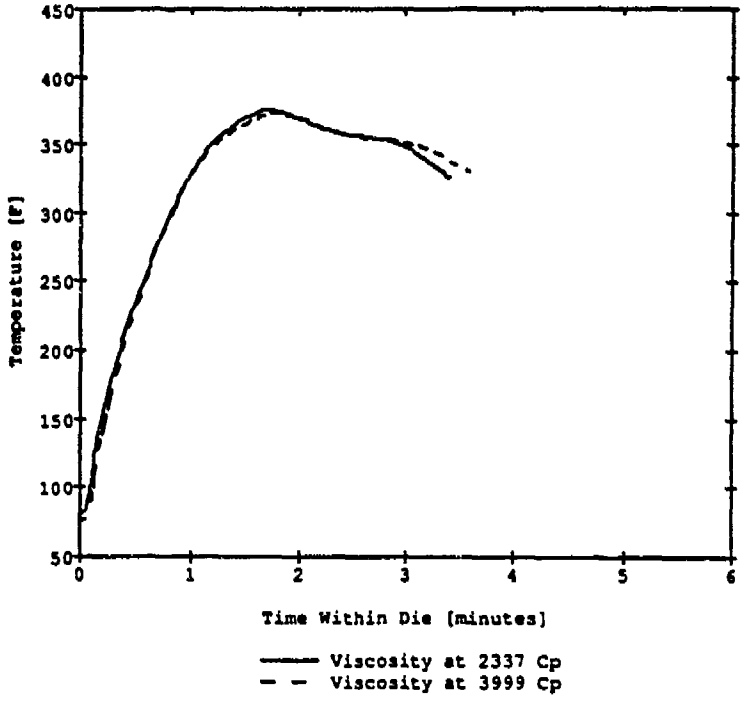

Figure 11. Temperature histories of stock pultruded at resin bath viscosity extremes.

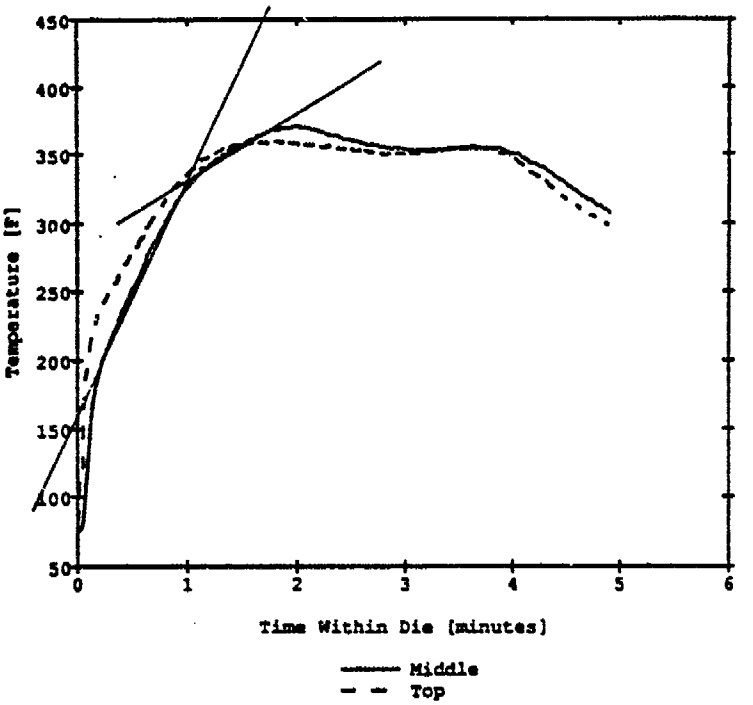

Figure 12. Representative time-temperature plot.

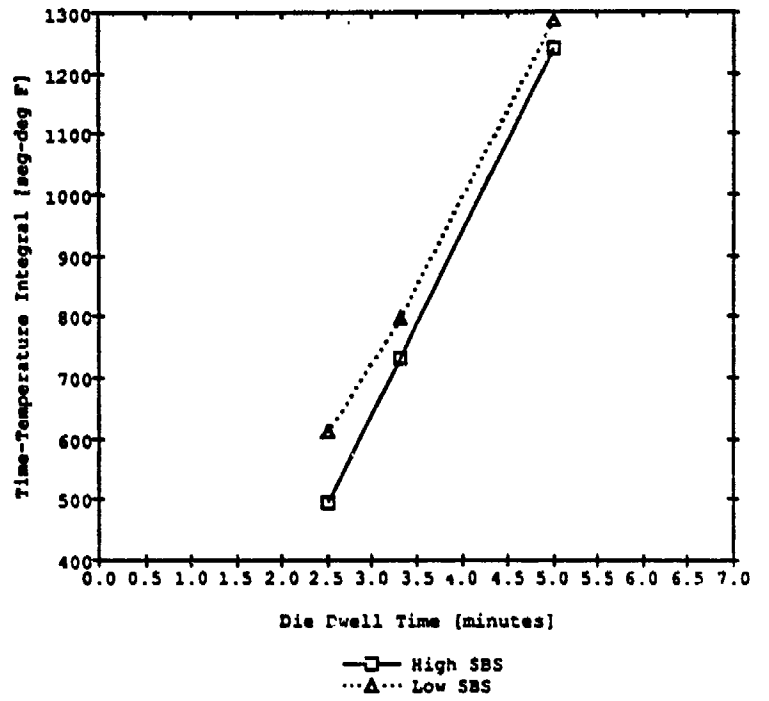

Figure 13. Values of temperature history curve integrations versus die dwell times.

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AN EXAMINATION OF PROCESSING VARIABLES IN THE PULTRUSION OF GLASS REINFORCEMENTS WITH AN EPOXY-ANHYDRIDE RESIN SYSTEM -
Donald J. Jaklitsch, Maria T. Bostic, and Elias R. Pattie

Technical Report MTL TR 91-53, December 1991, 27 pp - illus-tables, D/A Project 1L262105AH84

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Three stages of the pultrusion process were investigated for potential value in process control. Collectively, they represent the three major steps necessary for the manufacture of composite materials by pultrusion: fiber dispensation, resin application, and resin cure. The purpose was to determine whether the processing conditions imposed by each of these steps have a direct correlation to the physical properties exhibited by the final product. In order to examine the first two stages, a series of experiments were conducted involving the process components which precede the raw materials entry into the heated die. Specifically, these were the fiber tension as adjusted in the creels and the viscosity of the resin in the bath as a function of time. The third stage of the process was studied through a series of experiments designed to gauge the effect of varying the processing parameters associated with the heated pultrusion die which are the line speed and die temperature. The experimental results were evaluated by examining variation in mechanical properties of pultruded stock as produced under the various sets of conditions. Short beam shear and flexural tests were performed and measurements of product density, degree of cure, and void content were made. The results provide a solid empirical knowledge base for the process and a relative ranking of importance of the three stages in a control strategy.

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